Tight-Binding Quantum Chemistry Studies on Electrical Properties and Excited State Dynamics of Photofunctional Materials

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論文内容要旨

Nowadays the energy problem is the greatest challenge for mankind faced. Photoelectric effect provides a suitable approach to solve the energy problem by converting solar energy, an alternative energy source, to more convenient secondary energy. The performance of devices utilizing photoelectric effect strongly depends on the fundamental physical and chemical properties of photofunctional materials [1,2]. Therefore, it is not surprising that the field of photofunctional materials will remain at the forefront of both the academia and industry. Although experimental techniques gives highly accurate information, development and practical application of photofunctional materials nowadays is too complicated to be accomplished without knowing the structural, electronic and electrical properties of materials. Computational methods give us the essential information to understand the properties of materials and reducing production cost. However, high computational cost of conventional computational methods and the lack of effective theoretical tools for large-scale/periodic systems limited the study on realistic photofunctional material systems. In the present work, the aim is not only using developed computational tools to explore the fundamental optical, electronic and electrical properties, but also developing the efficient computational tool to study and understand excited state properties well including dynamics behavior of photofunctional materials.

Chapter 2 Computational Methods

Tight-binding quantum chemical molecular dynamics (QCMD) programs, "Colors", "Colors-excite" and the electrical properties simulator "Colors-cond", which realize over 5000 times acceleration compared to the conventional first-principle molecular dynamics method, were used to study the fundamental chemical and physical properties of photofunctional materials.

Chapter 3 Quantum Chemistry Study on Conduction Mechanism of n-Type Transparent Conducting Oxides

Indium tin oxide (ITO) is the most widely used photofunctional materials in many devices [3]. However, because of the complicated geometries and the lack of effective tools for studying excited state of large-scale/periodic systems, the effect of dopant and oxygen vacancies on the electronic, electrical properties and

conduction type of In_2O_3, was not well understood. To explore this effect, tight-binding quantum chemistry program working for large-scale/periodic systems was employed. Comparing the electrical conductivity of In_2O_3 with defects and impurities with that of undoped In_2O_3, it was clarified that In_2O_3 containing defects and impurities has the larger electrical conductivity. Fig. 1 shows PDOS of ITO. The obtained results show that the presence of higher valency dopant Sn atoms leads to the formation of impurity states lying just below the bottom of the conduction band and is helpful for the increase of conductivity of In_2O_3. The similar results were also observed from ITO with oxygen vacancies. UV-vis absorption spectra of ITO calculated by "Colors-excite" demonstrated that there is no absorption peaks in the whole visible region. The calculated electrical conductivity and UV-vis absorption spectrum proved that ITO has the simultaneous excellent conductivity and transparency. The successful study on the electrical and optical properties of n-type TCOs might suggest a way to explore and design potential homojunctional p-type TCOs based on In_2O_3.

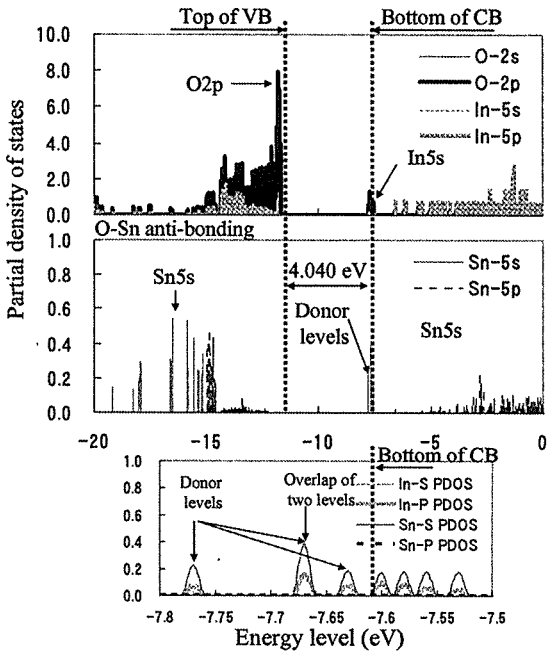

Fig. 1 PDOS of ITO.

Chapter 4 Quantum Chemistry Study on Conduction Mechanism of p-Type Transparent Conducting Oxides

Though Sn-doped In_2O_3 is the most widely used n-type TCOs, In_2O_3 based p-type TCOs materials are rarely known whereas such materials could open a way to widen a range of novel application. To study the effect of lower valency dopant on electronic and electrical properties of n-type In_2O_3 and analyze the reason of different conductivity of n- and p-type TCOs, tight-binding quantum chemistry calculation was performed. Contrary to ITO, from PDOS of large Zn-doped In_2O_3 (IZO) shown in Fig. 2, it became clear that due to the existence of the smaller radius acceptor-type impurity Zn, the acceptor-type impurity states were formed just above the top of valence band. The formation of accepter level leads to the p-type conductivity of IZO. Furthermore, by analyzing the process of electrical conductivity, the carrier concentration was found to dominate the electrical conductivity of IZO. This work

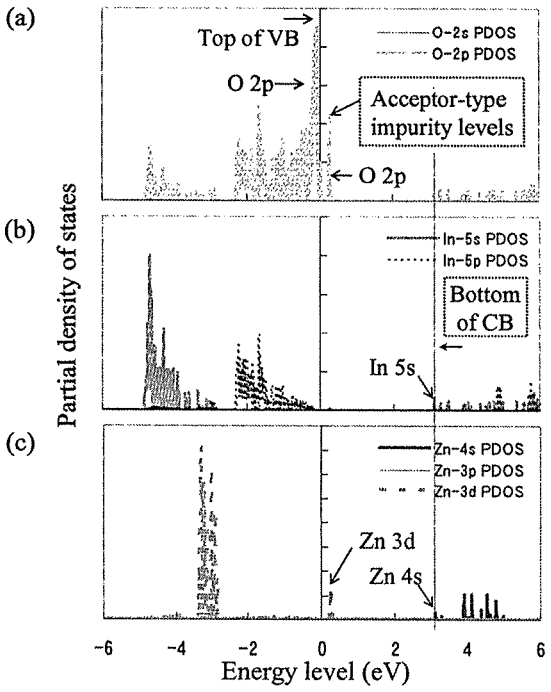

Fig. 2 PDOS of IZO

clarified the possible formation of In_2O_3 based n-p homojunctional photofunctional TCOs by providing different dopant sources. The main parameters that dominate the conductivity of n- and p- type TCOs were found out. It will widen the practical applications. My results obtained in Chapter 3 and Chapter 4 suggest that in-house tight-binding quantum chemical molecular dynamics method is very effective computational tool for developing and designing both n- and p-type TCOs with high calculation speed.

Chapter 5 Structural Effect on Electronic and Electrical Properties of Reactive Anatase(001) Surface

As the most reactive surface, anatase(001) surface attracted considerable attentions in many application fields. To find out the optimum anatase(001) surface, the UV-vis absorption spectrum of four surface models with different thickness and anatase bulk model were calculated by means of "Colors-excite" program for the first time and shown in Fig. 3. By combining "Colors-cond" program and Monte Carlo method, the thickness dependence of electrical properties, especially electron mobility of anatase(001) surface was achieved. The results have shown that anatase(001) surface with a thickness of 1.0 nm is promising for its application in photocatalyst and solar cell field. This study has revealed the structural influence of photofunctional materials on the electronic and electrical properties and thus will help to design new photofunctional materials. The optimum anatase(001) surface with a thickness of 1.0 nm will be used as substrate materials in Chapter 6.

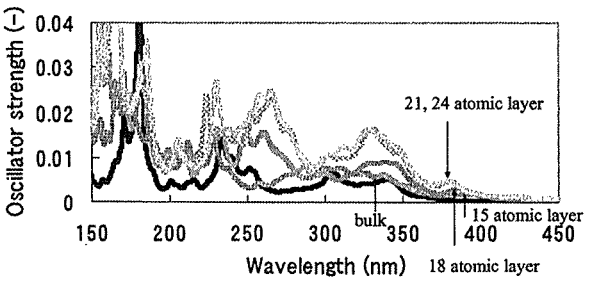

Fig. 3 Absorption spectra of anatase bulk and slabs

Chapter 6 Interfacial Electron Transfer Mechanism of Perylene with Acrylic Acid Sensitized Anatase(001)

The interfacial electron transfer in dye-sensitized anatase(001) plays a principal role in a variety of photoinduced reactions. However, the fundamental step involving the surface effect on the electron transfer from an adsorbate molecule to the most reactive anatase(001) host substrate is still poorly understood. In the present study, the most suitable adsorption mode (dissociative adsorption) and absorption spectra of PAA on anatase(001) was investigated by using in-house program, "Colors-excite". From Fig. 4, my finding that red-shift occurs when PAA adsorbed on anatase(001) suggests PAA/anatase(001) system is helpful to improve the long term stability of solar cell. Thus, this study suggests that anatase(001) maybe a very potential substrate for dye organic sensitizer than the most stable anatase(101). This study also proposed an effective computational tool "Colors-excite" to study electronic excitation properties for

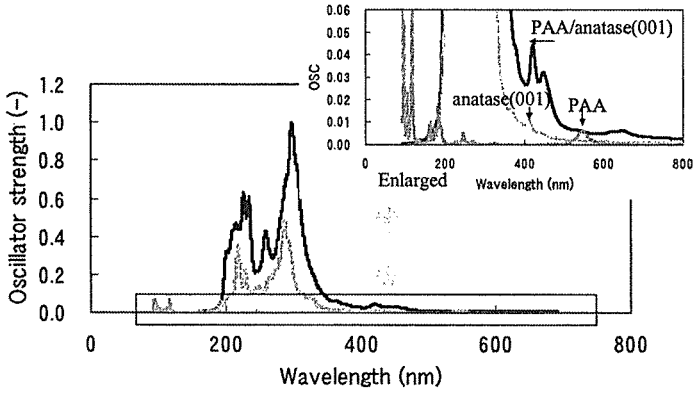

Fig. 4 Absorption spectrum of PAA/anatase(001) surface.

adsorbed large-scale systems.

Chapter 7 Quantum Mechanical and Molecular Dynamics Studies on Photooxidation Mechanism of Acetone on Anatase(001) Surface

As most used photocatalyst, the excited state property of TiO_2 is of importance. Even though there are a few theoretical tools for excitation calculation [4], it is still a difficult problem to study the dynamics behavior of excited state of large-scale/periodic systems. To theoretically explore the excited state dynamics behavior of hydrated anatase(001) surface and the possibility of photocatalytic oxidation of acetone on hydrated anatase(001), I focused on developing the computational tool "Colors-excite", which is expected to be efficient for the simulation of the dynamics behavior of both excited state and ground state of photofunctoinal materials. Fig. 5 shows the dynamics behavior of excited state of hydrated anatase(001) surface. This result indicates that active OH radicals were produced because of the significant increase of the distance between surface Ti and O increased to 1.93Å and the produced OH radicals are considered as reason of the photocatalytic oxidation of acetone on hydrated anatase(001) surface. Hence, for the acetone/hydrated anatase(001) system, the photocatalytic mechanism of acetone on anatase(001) is concluded that oxidation reaction is preferred than reduction reaction. This study proposes an alternative computational tool to study dynamics behavior of both excited state and ground state and it may be helpful to understand the photocatalytic oxidation process of other toxic organic compound on TiO_2 surface.

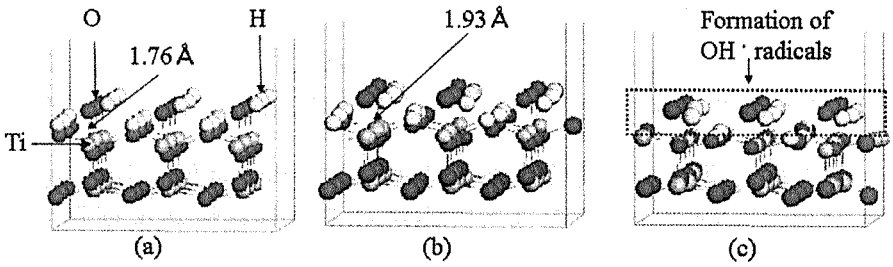

Fig. 5 Dynamics behavior of excited state of hydrated anatase(001) surface at (a) 0 step (b) 260 step, and (c) 300 step.

Chapter 8 Summary and Conclusions

By theoretically simulating the fundamental physical and chemical properties of different photofunctional materials, the efficient candidates to improve the performance of photocatalyst and solar cell which can effectively convert solar energy to more convenient secondary energy were proposed. Moreover, a potential computational tool which may be an alternative way to explore the electronic, electrical properties and dynamics behavior of large-scale/periodic materials that can reflect the realistic materials in both ground state and excited state was successfully developed.

References:

[1]. M. Fujita et al., Electron. Lett. **39** (2003) 24.

[2] K. L. Chopra et al., Thin Solid Films **102** (1983) 1.

[3]. F. H. Zhu et al., Thin Solid Films **359** (2000) 244.

[4]. R. J. Buenker et al., Theor. Chim. Acta. **39** (1975) 217.

論文審査結果の要旨

本研究は、光機能材料の物理・化学的性質のうち特に重要な性質である電子状態、光学特性、電気伝導特性および励起状態ダイナミクスに焦点をあて、光電子デバイスのプロセス・デバイス設計に資する指針を与える目的で理論的な研究を行ったものである。さらに、光機能材料の設計に資する現実的大規模系の解析のために、新規シミュレータを開発と応用にも挑戦している。

本論文は「Tight-Binding Quantum Chemistry Studies on Electrical Properties and Excited State Dynamics of Photofunctional Materials（光機能材料の電気特性および励起状態ダイナミクスに関する Tight-Binding 量子化学的研究）」と題し、以下の 8 章から成り立つ。

第 1 章では、光電作用を利用する各種光電子デバイスに用いられる代表的光機能材料における接合形成とその評価の重要性について説明し、光学、電子および電気伝導特性予測に関する既往の研究をまとめ、本論文の目的について述べている。

第 2 章では、本研究で用いている Tight-Binding 量子分子動力学法および第一原理量子化学の理論的背景について述べるとともに、Tight-Binding 量子分子動力学に基づき吸光スペクトルを推算する手法及び電気伝導度を推算する手法について説明している。

第 3 章では、Tight-Binding 量子分子動力学法を用いて、透明導電材料である ITO(Sn doped In_2O_3) に対する電子、光学、電気特性を解析している。母体 In_2O_3 中の Sn が酸素欠陥と複合してドナーとなることを示すとともに、n 型透明導電材料の伝導メカニズムを明らかにすることに成功している。

第 4 章では、ITO 中の Sn を Zn に置換した場合の効果を Tight-Binding 量子分子動力学法によって調べている。電子状態の解析結果から、Zn ドーピングにより p 型の伝導性が得られることが示唆された。さらに実際に電気伝導特性を調べることで伝導メカニズムの解明にも成功している。

第 5 章では、光触媒に用いられるアナターゼ TiO_2 の電子・光学特性を、Tight-Binding 量子分子動力学法を用いて解析している。TiO_2 の膜厚を変化させ、キャリア移動度、吸収スペクトルを評価した結果から、光活性の観点から最適な膜厚の存在を明らかにしている。

第 6 章では、色素増感型太陽電池用アナターゼ TiO_2(001)面における有機色素分子の結合モードを第一原理量子化学計算を用いて明らかにしている。さらに、Tight-Binding 量子分子動力学法を用いて、色素が吸着した TiO_2 表面の大規模系に対する光学特性を理論的に明らかにすることに成功している。

第 7 章では、大規模系における励起状態ダイナミクスを検討可能な独自のシミュレータを開発し、TiO_2 光触媒反応ダイナミクスへの応用に成功し、励起状態ダイナミクスの理論解析に基づく光触媒設計という新たな分野を拓くことに成功している。

第 8 章は、本論文の総括である。

以上、本論文は大規模系における電気特性および励起状態ダイナミクスを検討可能な新規手法を開発し、透明導電材料、光触媒、色素増感太陽電池を具体例としてその有効性を実証することに成功している。

よって、本論文は博士(工学)の学位論文として合格と認める。